THERMAL DIFFUSIVITY MEASUREMENTS OF CANDIDATE REFERENCE MATERIALS BY THE LASER FLASH METHOD

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ABSTRACT

The National Metrology Instituted of Japan (NMIJ) has been investigated the laser flash method in order to establish the thermal diffusivity standard of solid materials above room temperature. Uniform pulse heating technique, fast infrared thermometry and a new data analysis method were developed in order to reduce uncertainty in thermal diffusivity measurement. We are testing homogeneity and stability of candidate reference materials such as isotropic graphite to confirm their qualification as thermal diffusivity reference materials. Since graphite is not transparent to both heating laser beam and infrared light for thermometry, the laser flash method can be applied to graphite without black coatings. Thermal diffusivity values of these specimens with various thickness were measured with changing heating laser pulse energy. A unique thermal diffusivity value can be determined for homogeneous materials independent of the specimen thickness by extrapolating down to zero heating energy on the plot of apparent thermal diffusivity values measured with the laser flash method as a function of heating laser pulse energy.

KEY WORDS: thermal diffusivity; laser flash method; solid material; reference material

1. INTRODUCTION

The laser flash method is generally acknowledged as the standard and the most popular method to measure thermal diffusivity of solid materials above room temperature [1,2]. Because of the popularity of the laser flash method, there is an urgent need for reference materials for thermal diffusivity. Although several studies have been tried to establish reference materials for thermal diffusivity, as of now no reference material is available that is certified by official national and international organizations.

When thermal diffusivity is measured with the laser flash method, it is preferable that the material is optically nontransparent and dark colored (ideally black) in order to absorb the light of the pulse heating in a thin surface and to obtain high emissivity for radiative detection of transient temperature change after the pulse heating. From this point of view, carbon materials have been thought as candidates for reference materials of thermal diffusivity.

One candidate reference material for thermal diffusivity above room temperatures up to 2000 K is POCO AXM-5Q1 graphite. Round-robin measurement of thermal conductivity and thermal diffusivity of POCO AXM-5Q graphite were conducted under the auspices of AFML-AGARD from 1965 to 1972 and the recommended values were given [3]. Later on, several leading laboratories participated in a cooperative project under the auspices of CODATA to measure thermal diffusivity of POCO AXM-5Q1 graphite. However, POCO AXM-5Q1 graphite is not uniform enough since it was reported that thermal diffusivity of POCO AXM-5Q1 graphite is different more than 20 % for different specimens [4-7].

In the National Research Laboratory of Metrology (the predecessor of NMIJ), the grade GC-20 of glass like carbon was selected as a candidate of reference material for thermal diffusivity standard [8]. Glass like carbon is noncrystalline carbon produced by Tokai carbon Co. Ltd., Japan. However, since glass like carbon is very hard material, the method to cut and polish glass-like carbon to specimens suitable for laser flash method free from damage to the specimen surface has not been established.

Therefore, we have started to search reference material for laser flash measurement other than GC-20 glass like carbon and POCO AXM 5Q1. We have investigated homogeneity and stability of a number of graphite materials produced by different manufacturers to select a candidate for a thermal diffusivity reference material and a grade IG-110 produced by Toyo Tanso Co. Ltd. was selected.

In this paper, the study on thermal diffusivity measurement of IG-110 is reported.

2. MEASUREMENT

2.1 Measurement

The National Metrology Institute of Japan (NMIJ) has been studied the laser flash technique to establish the thermal diffusivity standard of solid materials above room temperature [8].

An advanced laser flash technique has been developed after technical improvements in order to make thermal diffusivity measurement under well-defined initial and boundary conditions as follows.

(i) Uniform pulse heating of a specimen by an improved laser beam using an optical fiber. (Reduction of the nonuniform heating error) [8,9]

(ii) Development of a fast infrared radiation thermometer with the absolute temperature scale. (Reduction of the nonlinear temperature detection error) [8,10]

(iii) Introduction of a new data analysis algorithm "a curve-fitting method" where the entire region of transient temperature curve is fitted by the theoretical solution under the real boundary condition. (Reduction of the heat loss error) [8,11]

Thermal diffusivity measurement was made using a laser flash instrument (LAF-502N, Kyoto Electronics Manufacturing Co., Ltd.) as shown in Fig. 1. This instrument was developed based on above technical improvements [12]. A specimen is set on a specimen holder placed at the center of a carbon/carbon composite heater inside a vacuum chamber. The chamber has a vertical cylindrical shape, a pulsed laser beam comes impinges on the front surface of the specimen through the top window and an infrared radiation thermometer observes the rear surface of the specimen through the bottom window. The specimen is supported by one ring in order to suppress heat loss to the specimen holder. There is a diaphragm above the specimen with the same aperture size to the specimen diameter. The Nd-YAG laser, wavelength is 1064 nm, is used for pulse heating the specimen. The Laser beam is homogenized through a step-index optical fiber and mode mixer in order to heat the specimen surface uniform. The transient temperature curve of the rear surface of the specimen is observed using an infrared radiation thermometer. Laser-pulse intensity is monitored by a photo-detector simultaneous with the transient temperature curve of specimen.

Measurement was carried out from room temperature to 1200 K.

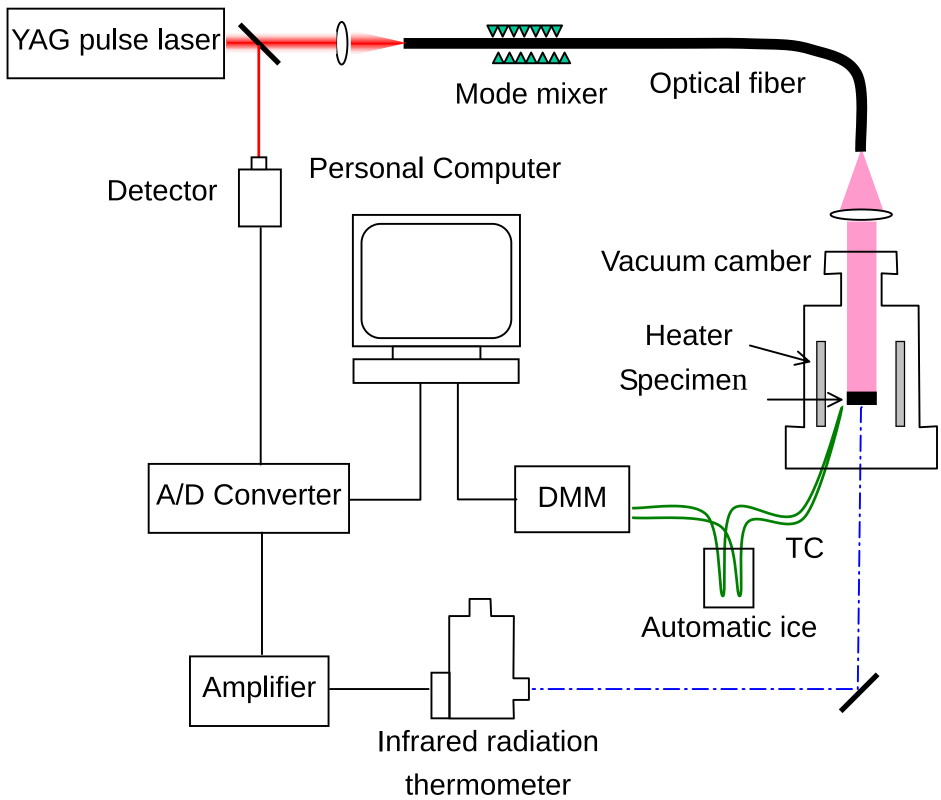

Figure 1. Schematic diagram of measurement system.

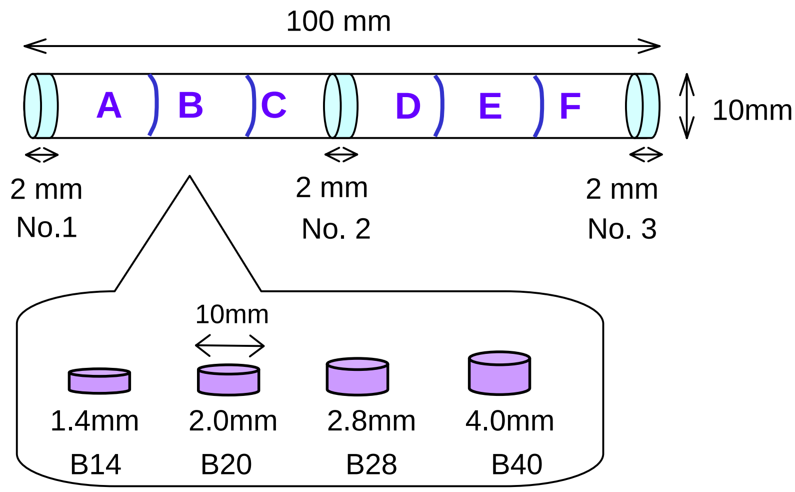

Figure 2. Sampling locations of specimens cut out of a rod of IG-110 graphite.

2.2 Specimens

IG 110 is a grade of isotropic high-density graphite manufactured by Toyo Tanso Co., Ltd. “IG-110” was selected as a candidate of thermal diffusivity reference material. NMIJ stocks 200 rods of IG-110 which are100 mm in length and 10 mm in diameter. We have prepared six specimen sets and three specimens from a rod as shown in Fig. 2. Each set includes four specimens that were 10 mm in diameter and 1.4mm, 2.0mm, 2.8mm and 4.0mm in thickness. Specimens were cut out from rods then polished to make both surfaces parallel. Thickness of specimens is measured using a linear gauge. Thickness variation of a specimen is several micrometers. These processes are necessary to define the specimen thickness with small uncertainty.

2.3 Analysis

The curve-fitting method [8,11] is used to calculate thermal diffusivity from the transient temperature curve obtained by the laser flash measurement. The entire set of the experimental data is fitted by Cape and Lehman’s theoretical curve [13] corrected by Josell et al. [14], which gives the analytical solution under the heat loss boundary condition. Both the thermal diffusivity and the Biot number are simultaneously determined by this curve fitting method.

One advantage of the curve-fitting method is that the quality of experimental data can be checked by observing the discrepancy between the experimental data and the theoretical curve. Data of poor quality such as those affected by nonuniform heating, by drift of the steady temperature or by a temperature-detection system of slow response time can be found immediately. Thus, only the experimental data of good quality are selected and the thermal diffusivity values with smaller uncertainty are obtained.

The origin of the time was set at the center of gravity of the observed laser-pulse intensity distribution when the observed transient temperature curve is fitted to a theoretical curve [15].

3. RESULTS AND DISCUSSION

Figure 3 shows an example of a transient temperature curve of IG-110 graphite at room temperature 25.6 °C. This "25.6 °C" is the steady temperature at this measurement. The temperature rises up to about 28 °C from 25.6 °C after heating by a laser pulse. Thermal diffusivity of this specimen is determined as 9.76×10^{-5} $m^2 s^{-1}$ at 25.6 °C from this curve based on the curve-fitting method. In Fig. 3, the steady temperature varies from 25.6 °C to 28 °C. The value of 9.76×10^{-5} $m^2 s^{-1}$ cannot be directly assigned to 25.6 °C because thermal diffusivity is a temperature dependent intrinsic property to each material and the steady temperature of the specimen rises during a measurement procedure. This value is some average of thermal diffusivity between 25.6 °C and 28 °C.

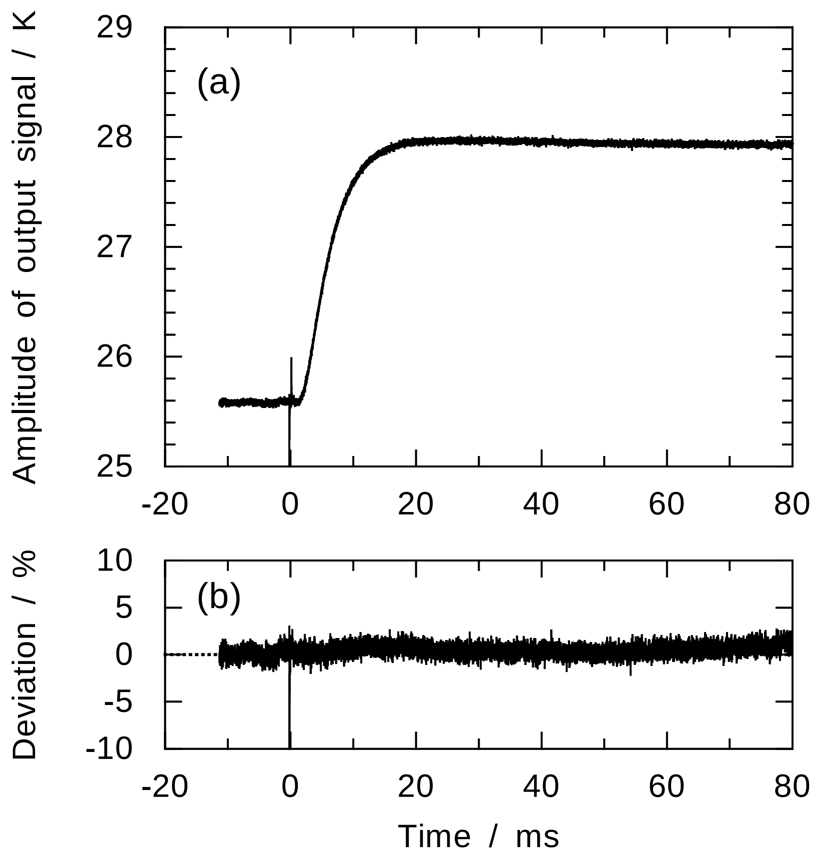

Figure 3. The transient temperature curve of rear surface at room temperature for the IG-110 specimen R2-E20. (a) experimental data, (b) deviation of the experimental data from the theoretical curve. This output signal is calculated in temperature from output signal of infrared radiation thermometer.

We have introduced a procedure to solve this problem. Apparent thermal diffusivity was measured for every specimen with changing heating laser pulse energy at a fixed steady temperature and plotted as a function of amplitude of output signal as shown in Figs. 4 and 5. The intrinsic thermal diffusivity at the steady temperature is the value extrapolated down to zero amplitude of the output signal. Figure 4 shows results for the IG-110 specimen R3-C14 at various levels of temperature. Thermal diffusivity at each fixed steady temperature is calculated by extrapolating procedure. For this specimen, the intrinsic thermal diffusivity values are 3.76 x 10^{-4} m^2 s^{-1} at 506 K, 2.66 x 10^{-4} m^2 s^{-1} at 816 K, 2.15 x 10^{-4} m^2 s^{-1} at 995 K and 1.84 x 10^{-4} m^2 s^{-1} at 1203 K, respectively.

Since thermal diffusivity is a physical property intrinsic to material, a unique thermal diffusivity value should be obtained independent of the specimen thickness of the same material. Figure 5 shows the signal amplitude dependence of thermal diffusivity of four specimens from the specimen set R3-C at 299 K. In fact, four extrapolated values agree within 5 %. A significant difference of thermal diffusivity value depend on specimen thickness could not be found, because heterogeneity of the IG-110 rod is as large as 5 % discussed in detail later.

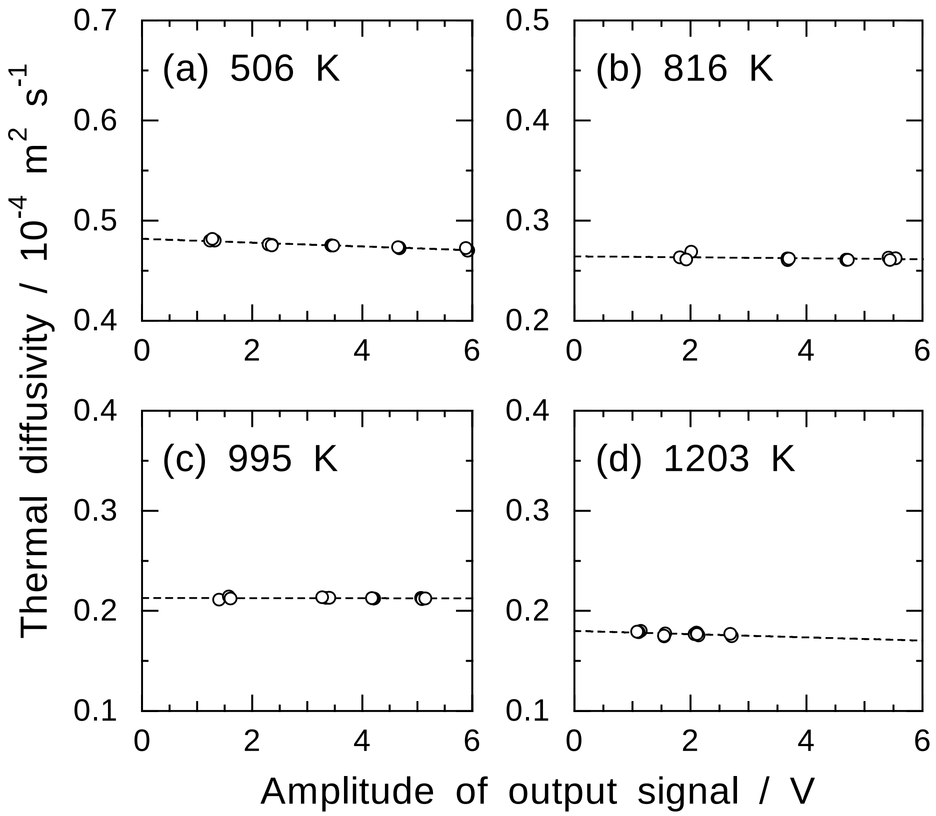

Figure 4. Heating laser pulse energy dependence of thermal diffusivity at various temperature for the IG-110 specimen R3-C14. (a) 506 K, (b) 816 K, (c) 995 K, (d) 1203 K. Value of horizontal axis is amplitude of output signal of infrared radiation thermometer.

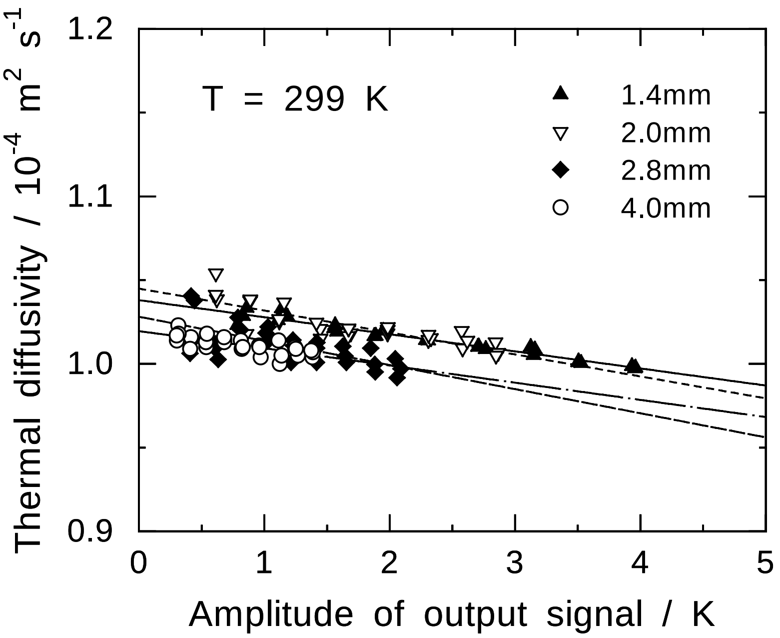

Figure 5. Heating laser pulse energy dependence of thermal diffusivity at room temperature for the IG-110 specimen set R3-C. Value of horizontal axis is amplitude of output signal of infrared radiation thermometer calculated in temperature.

If a set of reference specimens with various thickness of same material is available, laser flash thermal diffusivity measurement instruments can be calibrated systematically in wide range of response and temperature with systematically changing specimen thickness and heating pulse energy. If only one reference specimen is available, calibration is just effective to the specimen whose thermophysical property and dimensions are similar to the reference specimen.

The National Metrology Institute of Japan (NMIJ) has a plan to establish the SI traceable thermal diffusivity standard for solid materials above room temperature. All measuring units in the laser flash system should be calibrated traceable to the national standard. For example, time scale of data acquisition system for recording transient temperature curve was calibrated by a reference sign wave from a calibrated function generator.

Major sources of uncertainty in thermal diffusivity measurement are follows; (i) uncertainty of specimen thickness, (ii) uncertainty of time scale, (iii) uncertainty of pulse width [15,16], (iv) non-uniform heating effect [8,17], (v) heat loss effect [11], (vi) uncertainty of infrared radiation thermometry [10], (vii) drift of steady temperature, (viii) uncertainty of data analysis, (ix) uncertainty of extrapolation, (x) uncertainty of steady temperature measurement. Reference materials for thermal diffusivity should be stable for a long time, homogeneous and resistive to heat treatment unit. In order to make one-dimensional heat diffusion after a pulse heating, a reference material should be dense. Although the laser flash technique can be applied to transparent material if both surfaces are covered with black coating, the coating behaves as thermal resistance and introduces additional uncertainty in measurement. So, candidate of reference materials for laser flash thermal diffusivity measurement should have high absorbtance to the heating laser beam and high emissivity to radiative temperature detection in order to be measured without black coatings. Isotropic graphite such as IG-110 graphite meets these requirements.

We have investigated homogeneity and stability of IG-110 specimens to examine their qualification as thermal diffusivity reference materials. Figure 3(a) shows a typical transient temperature curve observed for the IG-110 specimen R2-E20 at room temperature. The output signal of the infrared radiation thermometer is converted to

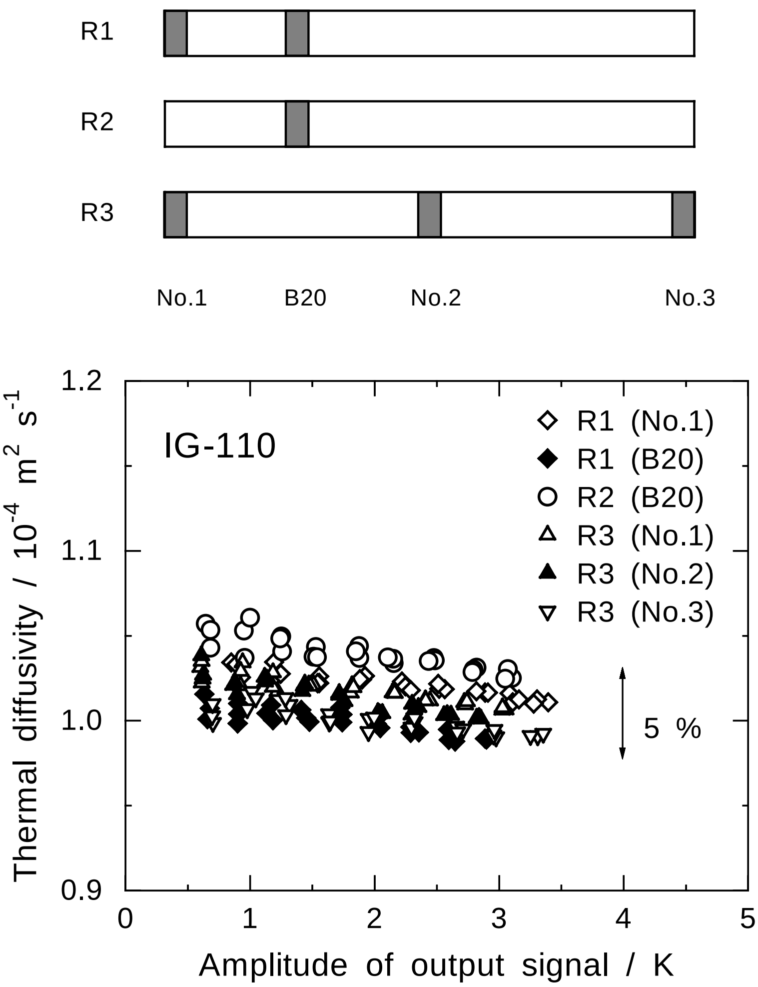

Figure 6. Heating laser pulse energy dependence of thermal diffusivity at room temperature of IG-110 specimens cut from three rods. The sampling locations of specimens are also exhibited. Value of horizontal axis is amplitude of output signal of infrared radiation thermometer calculated in temperature.

temperature based on the temperature scale calibrated by a black body furnace. The experimental data shows good signal to noise ratio. This curve was analyzed by the curve-fitting method to calculate thermal diffusivity.

The deviation of the experimental data from fitted theoretical equation is expanded and plotted in Fig. 3(b). The deviation is considerably small and calculated thermal diffusivity value is not sensitive to fitting area by the data analysis. Thus, the specimen is expected to be homogeneous enough for intrinsic thermal diffusivity to be defined. Figure 3 also demonstrates that measurement is made under the initial condition of rather uniform heating by pulsed laser beam and the boundary condition of small drift of temperature, and good temporal responsivity of a fast infrared radiation thermometer, and so on by using this instrument.

Figure 6 shows thermal diffusivity of IG-110 specimens at room temperature cut out from three rods. All specimens have the same shape of 10 mm in diameter and 2.0 mm in thickness. The sampling-locations of specimens are also shown in Fig. 6. Intrarod homogeneity can be estimated from the thermal diffusivity values of three specimens from R3. Interrod homogeneity can be estimated from the thermal diffusivity values of R1-No.1, R1-B, R2-B and R3-No.1. Figure 6 suggests that both intrarod and interrod heterogeneity of IG-110 are about 5 % and much smaller than heterogeneity of POCO-AXM5Q1 graphite of more than 20 % [4-7].

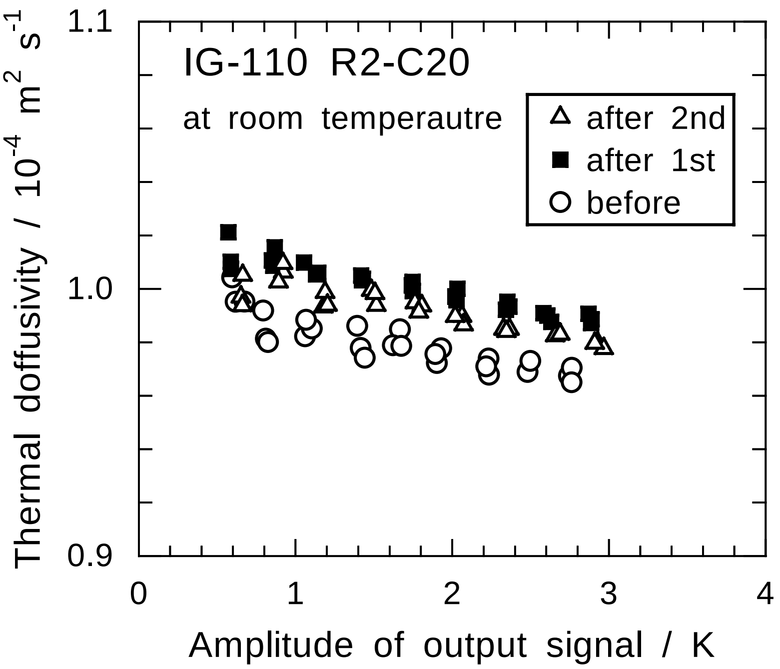

Figure 7. Heating laser pulse energy dependence of thermal diffusivity at room temperature for the IG-110 specimen R2-C20 after annealing at 800 ^{o}C for 4 hours in a vacuum. Value of horizontal axis is amplitude of output signal of infrared radiation thermometer calculated in temperature.

Since reference materials for laser flash measurement supposed to be used repeatedly, effect of heat treatment on IG-110 specimens should be checked. Figure 7 shows thermal diffusivity at room temperature after annealing at 800 ^{o}C for 4 hours in a vacuum. It is found that the thermal diffusivity of IG-110 increases after the first annealing and the change of thermal diffusivity by the first annealing was reproducible for a number of specimens. Piece to piece difference of thermal diffusivity value is reduced after annealing. Change by the second annealing is much smaller than the first change. Something like water absorbed by the process of cut and polish might explain the effect of annealing.

According to these experimental results, IG-110 is suitable for a thermal diffusivity reference material after the annealing.

4. CONCLUSION

We have been studying the laser flash method in order to establish the SI traceable thermal diffusivity standard. We have investigated IG-110 graphite as a candidate reference material. Thermal diffusivity values of IG-110 specimens with different thickness were measured with changing heating laser pulse energy. An intrinsic thermal diffusivity value can be determined for homogeneous materials independent of the specimen thickness by extrapolating down to zero heating energy on the plot of apparent thermal diffusivity values measured with the laser flash method as a function of heating laser pulse energy. It is found that IG-110 is qualified as a reference material after annealing process. Based on this research, we are preparing to supply IG-110 as thermal diffusivity reference material now.

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